SPIN-LATTICE RELAXATION IN ZERO-MAGNETIC FIELD INDUSED BY MOLECULAR REORIENTATIONS

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The stochastic Liouville method is used to analyze the general problem of spin-lattice relaxation in zero-field for molecules undergoing Markovian reorientations.

I. Introduction

The resolution advantage of zero-field (ZF) studies for orientationatty disordered materials is well known. In particular, the novel-pulsed ZF NMR and NQR technique [I,2] offers an excellent approach to this problem since it removes the orientational anisotropy which produces the broad high-field line shapes in solids. In ZF NMR and NOR the signal comes from longitudinal nuclear magnetization, i.e. the rank-I statisiical tensor. Time-domain ZF signals have also been observed using the method of perturbed angular correlations of γ-ray cascades [3]. From such experiments it is possible to extract information concerning the zero-field spin-lattice relaxation (ZF SLR) of rank ≥ 2 statistical tensors. The corresponding response function depends on the rates and microscopic details (in the slow-motional regime) of molecular reorientations which modulate the antisotropic part of the spin Hamiltonian.

Mathematical techniques have recently been developed which make analyses of ZF NMR spectra in the complete tumbling regime feasible [4-6]. Our purpose here is to extend this theory. We present a general formalism which enables us to compute the response function of statistical tensors of arbitrary rank-k irrespective of the models used to describe the Markovian molecular reorientations. A compact expression for the correspondtng spectral function is obtained, which is valid for the complete tumbling regime. To illustrate the use of the theory we calculate the rank-2 perturbation coefficient of γ-ray cascades arising from the quadrupole interaction of a spin-1 nucleus with an axially symmetric electric field gradient. All the calculations in this paper are confined to situations that are macroscopically isotropic. There is continuity with the formalism of the preceding articles [4-6] and intermediate results

derived there are assumed to have been looked at by the reader.

2. Theory

In ZF the spin Hamiltonian for the problem is

$$\hat{H}(\Omega) = \sum_{q,p}(-1)^p \hat{F}_{2p} D^2_{q-p}(\Omega) A_{2q} \tag{1}$$

Here $\hat{F}_{2p}$ is the p-component of a second-rank spin tensor operator in the laboratory frame. A_{2q} are components of a ZF splitting tenser expressed in the molecular coordinate system(the principal axis frame) and $D^2_{q-p}(\Omega)$ are the Wigner rotation matrices describing the transformation between the two frames. The explicit form of $\hat{F}_{2p}$ and A_{2q} will depend on the type of interaction.

For sufficiently large molecules in dense media the stochastic reorientational process may be assumed to be Markovian. It then follows that an appropriate ensemble average spin density operator $\hat{\rho}(\Omega, t)$ obeys the stochastic Liouville equation (SLE) [7,8]

$$\frac{\partial \hat{\rho}(\Omega, t)}{\partial t} = -iH^x \hat{\rho}(\Omega, t) + \hat{\hat{L}}_\Omega \hat{\rho}(\Omega, t) \tag{2}$$

where $H^x \hat{\rho} = [\hat{H}, \hat{\rho}], \hbar = 1$ and $\hat{\hat{L}}_\Omega$ is the stationary Markovian operator describing the tumbling process. Eq.(2) must be solved with the initial condition

$$\hat{\rho}(\Omega, 0) = \phi(\Omega)\hat{\rho}(\Omega) = \frac{\hat{\rho}(0)}{8\pi^2} \tag{3}$$

which takes into account the fact that for isotropic systems there is an equilibrium distribution of molecular orientations $\phi(\Omega) = \frac{1}{8\pi^2}$

The status of the spin ensemble can be discussed in terms of statistical tensors $\rho^{(kp)}$(i.e. state multipole moments)

$$\hat{\rho}(\Omega, t) = \sum_{k,p} \rho^{(kp)}(\Omega, t)\hat{T}_{kp}(I) \tag{4}$$

where the coefficient $\rho^{(kp)}(\Omega, t)$ and the irreducible polarization operator $\hat{T}_{kp}(I)$ [9] are given by

$$\rho^{(kp)}(\Omega, t) = Tr[\hat{\rho}(\Omega, t)\hat{T}^+_{kp}(I)],$$

$$\hat{T}_{kp}(I) = \left(\frac{2k+1}{2I+1}\right)^{1/2} \sum_{mm'} C^{Im'}_{Im\,kp} |Im'\rangle\langle Im| \tag{5}$$

Here $C^{Im'}_{Im\,kp}$ is a Clebsch-Gordan coefficient. The corresponding response and spectral functions, $G^{kp}(t)$ and $\tilde{G}^{kp}(s)$, are obtained as averages over the equilibrium (isotropic) distribution:

$$G^{kp}(t) = \int d\Omega \rho^{kp}(\Omega, t), \tag{6}$$

$$\tilde{G}^{kp}(s) = \int_0^\infty G^{kp}(t) \exp(-st) dt, \tag{7}$$

where the tilde denotes Laplace transformation.

It thus follows from eqs. (5) and (6),(7) that

$$G^{kp}(t) = Tr(\int d\Omega \hat{D}(\Omega)\hat{\rho}(\Omega)\hat{D}^{+}(\Omega) \sum_q (-1)^p D^k_{q-p}(\Omega))\hat{T}_{kq}(I) \equiv \sum_q Tr[\hat{\sigma}^{kp}_q(t)\hat{T}_{kq}(I)] \tag{8}$$

where $\hat{D}(\Omega)$ is the finite rotation operator. Following refs. [4,10], we multiply both sides of eq.(2) by $\hat{D}(\Omega)$ on the left and by $(-1)^p \hat{D}^{+}(\Omega) D^k_{q-p}(\Omega)$ on the right. In isotropic systems this procedure allows integration over Ω in the general form as reported in ref. [10]. Through a straightforward extension of the derivation described in ref. [10] we obtain a compact differential kinetic equation

$$\dot{\hat{\sigma}}^{(kp)}_q(t) = -iH^x(0)\hat{\sigma}^{(kp)}_q(t) - \tau^{-1}\left(\hat{\sigma}^{(kp)}_q(t) - \sum_{q_1} \hat{\hat{P}}^{(k)}_{qq_1} \hat{\sigma}^{(kp)}_{q_1}(t)\right), \tag{9}$$

where τ is the mean lifetime between rotational jumps,

$$H^x(0) = \sum_\mu (-1)^\mu F^x_{2\mu} A_{2-\mu} \tag{10}$$

$$\hat{\hat{P}}^{(k)}_{qq_1} \hat{\sigma}^{(kp)}_{q_1}(t) = \int \hat{D}(\tilde{\Omega}) \hat{\sigma}^{(kp)}_{q_1}(t) \hat{D}^{+}(\tilde{\Omega}) D^k_{qq_1}(\tilde{\Omega}) f(\tilde{\Omega}) d\tilde{\Omega}, \tag{11}$$

where $\tilde{\Omega} = \Omega - \Omega'$ (see also refs. [4,10]). The initial condition for eq. (9) is obtained from eqs. (3), (4) and (8):

$$\hat{\sigma}^{(kp)}_q(0) = \frac{\rho^{(kp)}(0)\hat{T}^{+}_{kq}}{2k+1} \tag{12}$$

Formally eq. (9) is similar to the impact equation which describes gas-phase relaxation. Reorientations may be classified as either "weak" or "strong" depending on the angular jump, with its size set by the function $f(\Omega)$. The new formulation of the problem allows a solution irrespective of this circumstance in the general form.

From that purpose let us re-express $\hat{\sigma}_q^{(kp)}$ in the form

$$\hat{\sigma}_q^{(kp)}(t) = \sum_{KQ} [\sigma_q^{(kp)}(t)]_{KQ} \hat{T}_{KQ}(I) \tag{13}$$

It is easy to see that in this representation the response function can be written as

$$G^{(kp)}(t) = \sum_q (-1)^q [\sigma_q^{(kp)}(t)]_{k,-q} \tag{14}$$

Then we have, using vector notation,

$$\dot{\mathbf{X}}(\mathbf{t}) = -(\mathbf{i}\hat{\hat{\mathbf{\Lambda}}} + \hat{\hat{\ }})\mathbf{X}(\mathbf{t}) \tag{15}$$

where the column vector $\mathbf{X}(\mathbf{t})$ is constructed from the coefficients $\sigma_q^{(kp)}(t)]_{KQ}$. The elements of the evolution, $\hat{\hat{\mathbf{\Lambda}}}$, and the motivational, $\hat{\hat{\ }} = (\mathbf{1} - \hat{\hat{\mathbf{P}}}/\tau$, operator matrices are [9]

$$\hat{\hat{\Lambda}}^{qq_1}_{KQ\,K_1Q_1} = Tr(\hat{H}(0)[\hat{T}_{K_1Q_1}(I), \hat{T}^+_{KQ}(I)])\delta_{qq_1} =$$

$$\sum_{K'Q'} (-1)^Q (K_1Q_1; K-Q)^{K'Q'} Tr(\hat{H}(0)\hat{T}_{K\prime Q\prime}(I))\delta_{qq_1} \tag{16}$$

$$\hat{\hat{\ }}^{qq_1}_{KQ\,K_1Q_1} = \sum_{LMN} W^{(L)}_{MN} C^{LM}_{kq\,KQ} C^{LN}_{kq_1\,K_1Q_1} \tag{17}$$

where

$$(K_1Q_1; K-Q)^{K'Q'} \equiv (-1)^{2I+K'}[(-1)^{K+K_1+K\prime} - 1][(2K+1)(2K_1+1)]^{1/2} \times$$

$$\times C^{K'Q'}_{KQ\,K_1Q_1} \left\{ \begin{array}{ccc} K & K_1 & K' \\ I & I & I \end{array} \right\} \tag{18}$$

$$W^{(L)}_{MN} = (\delta_{MN} - A^{(L)}_{MN}), \quad A^{(L)}_{MN} = \int f(\tilde{\Omega}) D^L_{MN}(\tilde{\Omega}) d\tilde{\Omega} \tag{19}$$

To derive eq.(17) we have used the Clebsch-Gordan series for the product of Wigner matrices [9]. Eq.(15) can be solved by Laplace transformation to give

$$\tilde{\mathbf{X}}(s) = \hat{\hat{\mathbf{M}}}^{-\mathbf{1}}(s)\mathbf{X}(0) \tag{20}$$

where $\mathbf{M}(s) = s\hat{\hat{\mathbf{1}}} + i\hat{\hat{\mathbf{\Lambda}}} + \hat{\hat{\cdot}}$. It is easy to see from eqs. (12) and (13) that in this representation

$$\mathbf{X}(0) = [\sigma_q^{kp}(0)]_{KQ} = \left\{(-1)^q \frac{\rho^{(kp)}(0)}{2k+1}\delta_{Kk}\delta_{q,Q}\right\} \tag{21}$$

Eq.(20) is particularly suitable for numerical computation of the spectral function (7). The key step in the calculation is the inversion of matrix $\hat{\hat{\mathbf{M}}}$: '

$$\tilde{G}^{(kp)}(s) = \sum_{qq_1}(-1)^{q+q_1}[\hat{\hat{\mathbf{M}}}^{-1}]^{qq_1}_{k-q,k-q_1}\frac{\rho^{(kp)}(0)}{2k+1} \tag{22}$$

Since $\hat{\hat{\mathbf{M}}}$ has finite dimensions the inversion is readily achieved by standard techniques. The result of eq.(21) provides a general recipe for calculating the response of the rank$-k$ statistical tensor on Markovian molecular reorientations in ZF. The most severe restriction of the model is that the lattice is described only in terms of the orientationat degrees of freedom.

In the case osotropically rotating molecules, $f(\tilde{\Omega}) = f(cos(\tilde{\beta}))/4\pi^2$, from (17) and (19) we obtain

$$^{qq_1}_{KQ\ K_1Q_1} = \sum_L \tau_{\theta L}^{-1} C^{L0}_{kq\ K-q} C^{L0}_{kq_1\ k-q_1}\delta_{KK_1}\delta_{q-Q}\delta_{q_1-Q_1} \tag{23}$$

where $\tau_{\theta L}^{-1} = WL_{00}$ is the orientational relaxation time of the axial $L-$rank tensor. To illustrate the use of the theory we consider the case where the dominant anisotropic part of the spin Hamiltonian is the axially symmetric quadrupote interaction [5]:

$$\hat{H}(0) = \sqrt{\frac{2}{3}}D_Q K_I \hat{T}_{20}(I) \equiv \sqrt{\frac{2}{3}}\frac{eQV_{zz}}{2I(2I-1)}K_I\hat{T}_{20}(I) \tag{24}$$

where Q is the nuclear quadrupole moment,

$$K_I = (-1)^{2I}[\frac{1}{30}I(I+1)(4I^2-1)(2I+3)]^{1/2} \tag{25}$$

As follows from (16), (18) and (23)

$$\hat{\hat{\Lambda}}^{qq_1}_{KQ\ K_1Q_1} = (-1)^{2I+K}[\frac{10}{3}(2K_1+1)]^{1/2}D_Q K_I C^{KQ}_{K_1Q\ 20}\left\{\begin{array}{ccc} 2 & K & K_1 \\ I & I & I \end{array}\right\}[(-1)^{K+K_1}-1]\delta_{qq_1}\delta_{QQ} \tag{26}$$

As can be seen from (22) and (25) the components $[\sigma_q^{(kp)}]_K - q$ are uncoupled from the rest of the vector $\mathbf{X}$ and the problem reduces to the inversion of the matrix $\mathbf{M}$ in "Kq" subspace. It is convenient to calculate $\tilde{G}^{kp}(s)$ in the basis of eigenfunctions of the operator $\hat{\hat{}}$. In the "Kq" subspace we have

$$[\hat{\hat{\mathbf{U}}}^{-1}\hat{\hat{\Lambda}}\hat{\hat{\mathbf{U}}}]_{Kn\,K_1n_1} = {}'_{Kn\,K_1n_1} = \gamma_n\delta_{KK_1}\delta_{nn_1}, \quad \hat{U}_{Kq\,Kn} = C^{n0}_{kq\,K-q} \tag{27}$$

$\hat{\hat{U}}$ is the unitary matrix which makes the submatrix $[']^{qq_1}_{K-q\,K-q_1}$ in (22) diagonal, $\gamma_n = \tau_{\theta n}^{-1}$ denotes the eigenvalues. It is easy to see that in this representation eqs. (14) and (21) give

$$\tilde{G}^{(kp)}(s) = \left[\frac{1}{s\hat{\hat{\mathbf{1}}} + i\hat{\hat{\mathbf{\Lambda}}}' + \hat{\hat{}}}\right]_{k0,k0} \rho^{(kp)}(0), \tag{28}$$

where .

$$\hat{\hat{\Lambda}}'_{Kn\,K_1n_1} = (-1)^{2I+k}2D_QK_I\left[\sqrt{\frac{2}{3}}(2K+1)(2K_1+1)(2n+1)(2N_1+1)\right]^{1/2} \times$$

$$\times C^{20}_{n0\,n_10}\left\{\begin{array}{ccc} K & K_1 & 2 \\ I & I & I \end{array}\right\}\left\{\begin{array}{ccc} K & K_1 & 2 \\ n_1 & n & k \end{array}\right\}(\delta_{KK_1+1} + \delta_{KK_1-1}) \tag{29}$$

Consequently only one element of the inverted matrix $(\hat{\hat{\mathbf{M}}})^{-1}$ is needed to calculate the spectral function.

3. Discussion

In the fast motional limit, $D_Q\tau_{\theta 2} \ll 1$, taking into account (26)-(28) to second order in perturbation theory, we have

$$G^{(kp)}(s) = (s+\lambda_k)^{-1}\rho^{(kp)}(0), \quad G^{(kp)}(t) = \exp[-\lambda_k t)\rho^{(kp)}(0)$$

where

$$\lambda_k = \frac{3}{80}(eQV_{zz})^2\tau_{\theta 2}\frac{k(k+1)[4I(I+1) - k(k+1) - 1]}{I^2(2I-1)^2}$$

in agreement with Abragam and Pound[11]

For a simple illustration of the formalism introduced in section 2 we consider a case with $I = 1$. From (26)- (28) we obtain

$$\tilde{G}^{1p}(s) = \frac{(s+\tau_{\theta 2}^{-1})^2 + \frac{1}{3}D_Q^2}{s[(s+\tau_{\theta 2}^{-1})^2 + D_Q^2] + \frac{2}{3}D_Q^2\tau_{\theta 2}^{-1}}\rho^{1p}(0) \tag{30}$$

$$\tilde{G}^{2p}(s) = \rho^{2p}(0)\frac{N_1(s)}{sN_1(s) + N_2(s)}, \tag{31}$$

where

$$N_1(s) = \frac{1}{7}D_Q^2(s+\tau_{\theta 4}^{-1}) + \frac{16}{35}D_Q^2(s+\tau_{\theta 2}^{-1}) + (s+\tau_{\theta 2}^{-1})^2(s+\tau_{\theta 4}^{-1})$$

$$N_2(s) = \frac{2}{5}D_Q^2(s+\tau_{\theta 2}^{-1})(s+\tau_{\theta 4}^{-1})$$

Eq. (30) is identical to there suh of ref. [5](eq.(24)) which describes the ZF NMR spectral function [1,2]. Ordinary NMR coils can only detect rank-1 tensors. However, by experimental observaiion of γ-ray cascades, it is possible to extract information concerning the relaxation of $k \geq 2$ statistical tensors. In particular, the measurer anisotropy [3, 11, 12] is proportional to $G^{k0}(t)$. Sometimes it is convenient to observe the average correlation of all decays:

$$G^{k0}(\infty) = \tau_N^{-1}\int_0^\infty G^{k0}(t)\exp(-\frac{t}{\tau_N}),$$

which is just the Laplace transformation at $s = \tau_N^{-1}$, where τ_N is the mean nuclear lifetime.

The spectral function (30) depends on $\tau_{\theta 2}$ and $\tau_{\theta 4}$. In the "strong collision" model $f(\Omega) = \frac{1}{8\pi^2}$ and $\tau_{\theta 2} = \tau_{\theta 4} = \tau$. In contrast, $\tau_{\theta n}^{-1} = n(n+1)D_r$ under Debye orientational diffusion with coefficient D_r. Thus in the slow tumbling regime the precise form of the angular correlation depends on dynamical details of the motion.

It is interesting to compare our exact result (30) with the approximate analytical solution of the problem which has been obtained by Linden-Bell [12]. It is easy to see (by Laplace transformation of thc corresponding expressions for $G^{20}(t)$ which have been given in ref.[12] that in the fast motional regime our results coincide. However, her approximation is not sufficient to obtain good quantitative agreement wich eq. (30) in the slow-motional limit, when $D_Q\tau_{\theta 2} \simeq 1$.

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